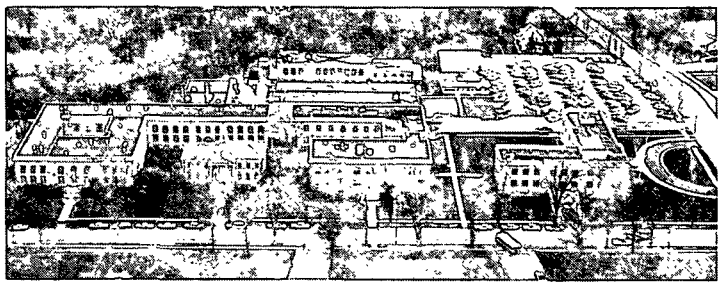

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 95

THE EFFECT OF AN ENZYMATIC SLIME CONTROL AGENT MX–1361 ACTIVATED SLUDGE TREATMENT PLANTS

THOMAS W. JOYCE, EUGENE F. ZANELLA, HARDEV S. DUGAL
AND HERBERT J. HATCHER

MAY, 1980

The Effect of an Enzymatic Slime Control Agent MX-1361 on Activated Sludge Treatment Plants

Thomas W. Joyce
Eugene F. Zanella
Hardev S. Dugal
Environmental Sciences Division
The Institute of Paper Chemistry
Appleton, Wisconsin 54911

Herbert J. Hatcher
Scientist
Economics Laboratory
St. Paul, Minnesota

ABSTRACT

Slime control in the paper mill is a major operational problem and expense facing paper companies. At present, slimes are controlled with synthetic organic chemicals, many of which contain heavy metals or are highly halogenated and are currently the focus of regulatory scrutiny.

An enzyme preparation MX-1361 has been developed to "control" slimes in pulp and paper mills. The mode of action of the enzyme is to cleave carbohydrate bonds in the bacterial slime, thereby dissipating it. There is a concern, however, that the enzyme might create problems either by deflocculating the bacterial flocs in the waste treatment plant or by exerting toxicity in the biologically treated effluent.

The conclusions of this study were:

1. The concentration of BOD and suspended solids in the treated effluent and the settling properties of the activated sludge are not affected by the addition of the enzyme.
2. No acute toxicity, as measured with Daphnia, was found in the treated effluents.

This enzyme preparation appears to have no effect on the operation or effluent characteristics of activated sludge systems. Apparently, the enzyme has been biologically oxidized because

tests specific for the enzyme showed no enzyme in the treated effluent.

INTRODUCTION

Recent concerns over the presence of toxic compounds in the environment have been widely publicized. These concerns emanate from the knowledge that a few toxic compounds are very recalcitrant to biodegradation and have the potential of bioaccumulation in the environment. The end result of this bioaccumulation has not been well documented in most cases, but it is generally believed to have an adverse impact on the environment. For these reasons, there is a growing concern that the currently used slimicides may not be acceptable to regulatory agencies in the near future.

Operation of most paper mills would be virtually impossible without the use of chemicals to control slime formation. The very characteristics which make desirable slimicides, high toxicity and slow biodegradability, are the same characteristics which attract regulatory attention. There would, obviously, be less regulatory agency concern with a slimicide derived from a natural product that would be easily biodegradable.

Economics Laboratory has developed an enzyme preparation, designated MX-1361, which could be used as a slime control agent. It disrupts the bacterially produced slime which concentrates

particulates and microbes that form a deposit. Because of the mode of action of the enzyme, i.e., cleaving carbohydrate bonds in bacterial slimes, the enzyme has the potential to disrupt bacterial flocs in the waste treatment plant as well. If this were to occur, the effluent suspended solids and effluent BOD might rise to unacceptable levels, and also the settling characteristics of the sludge might deteriorate to the point of process failure.

The objectives of this study were to:

1. Determine if the activated sludge process is affected by the addition of MX-1361, and,
2. Determine if the treated effluent contains toxicity attributable to MX-1361.

The approach taken to meet these objectives was to treat a sulfite-alkaline chemimechanical pulp mill effluent in bench scale activated sludge reactors and to monitor process performance and sludge settling characteristics. One reactor was operated on mill effluent taken before entering the mill's biological treatment plant. Another reactor was operated on the same effluent supplemented with active MX-1361 enzyme preparation. A third reactor was operated on the effluent supplemented with heat inactivated MX-1361 enzyme preparation. Inactive enzyme was also used because the enzyme is a protein and could create effluent toxicity without affecting the activated sludge process.

The treatment conditions were identical in each of the bench scale units and were chosen to be similar to the oxygen-activated sludge plant at the mill. The level of MX-1361 was selected to simulate normal operation throughout the paper mill supplemented by a spill of MX-1361 in one paper machine. Thus, considering both the addition of MX-1361 just prior to biological treatment and the simulated spill, this is probably the highest concentration of MX-1361 that would enter the treatment plant.

The bench scale activated sludge reactors were run for 31 days. The nominal hydraulic residence time (HRT) was 6 hours, and the nominal mean cell residence time (MCRT) was 8 days. Both of these conditions are typical of operating treatment plants in the pulp and paper industry. Throughout the course of the study, the effluent characteristics and sludge settling properties were monitored. A test for acute toxicity, as measured with Daphnia, was also performed.

RESULTS AND DISCUSSION

At the nominal MCRT of 8 days, 31 days operation was more than sufficient time to attain steady-state conditions. No significant operating problems were encountered after adjustment of the HRT.

Initially, the HRT was set at 3 hours to correspond with the HRT in the mill's aeration tank. However, the clarifiers on the bench scale units were not large enough to handle the flow, and it was necessary to increase the nominal HRT to 6 hours. Thus, instead of attempting to mimic treatment conditions at the mill, we attempted to simulate treatment effect, i.e., the removal of BOD and suspended solids.

Presented in Table 1 is a summary of reactor effluent characteristics. Also included is selected operating data from the mill wastewater treatment plant for comparison.

The data show that there was no difference in the effluent characteristics of the three bench scale activated sludge systems. Further, all three reactors were operating well within the bounds of typical effluent permits issued by regulatory agencies. Comparison of the bench scale reactor data with the full scale treatment plant shows that the reactors were treating the mill effluent at a slightly higher efficiency. This is expected since there is usually more control over bench scale units, and corrective actions can be taken quicker than on full scale plants.

A summary of the activated sludge settling data is presented in Table 2. The data show that there is no difference in either the initial settling velocities (ISV) or sludge volume indices (SVI) for the bench scale reactors. The ISV is a measure of how rapidly the sludge will settle, while the SVI is a measure of how

difference in the settling properties of these sludges. MX-1361 apparently has no effect on the settling properties of activated sludge.

The last issue to be resolved was related to effluent toxicity. There was a concern that either the enzyme or the stabilizers in the enzyme preparation might be toxic. Accordingly, static, acute bioassays with Daphnia magna neonates were performed on the treated effluents and also on active MX-1361 enzyme preparation at a concentration of 400 units/gallon. A summary of test conditions for these assays is presented in Table 3. An analysis of the data from these assays revealed EC50 values greater than 100% by volume in all cases. This means that no acute toxicity, as measured with Daphnia, was present in any of the treated effluents or in the MX-1361 enzyme preparation diluted to 400 units/gallon.

The last task undertaken was to determine if MX-1361 could be detected in the effluent from the reactors. A low enzyme activity in the feed to the bench scale reactors was reported, but there was none in the effluent. Either the enzyme had been inactivated by the strong oxidizing conditions in the reactor or it has been biologically degraded.

TABLE 2

Sludge Settling Data

REACTOR	ISV[a], ft/hr	SVI[b], mls/g
No Enzyme	3.7 ± 0.3	62 ± 8
Active Enzyme	3.9 ± 0.4	64 ± 6
Inactive Enzyme	3.7 ± 0.1	60 ± 4
Mill — operating data	5.8 ± 1.7	61 ± 19

a. Initial settling velocity

b. Sludge volume index

TABLE 3

Summary of Test Conditions for Daphnia magna Neonates

Sample Source	pH	Dissolved Oxygen, mg/L	Temp. °C	EC_{50} % Volume
No Enzyme Reactor				
mean initial	7.9	8.5	19.0	
mean final	7.9	6.6	21.0	>100
Active Enzyme Reactor				
mean initial	8.0	9.3	19.0	
mean final	7.9	7.4	21.0	>100
Inactive Enzyme Reactor				
mean initial	7.8	7.8	19.0	
mean final	7.8	6.4	21.0	>100
MX-1361 Enzyme Preparation				
mean initial	7.7	7.4	21.0	
mean final	7.9	7.5	21.0	>100

CONCLUSIONS

It can be concluded from this laboratory study that:

1. Enzyme MX-1361 does not affect the operation of activated sludge systems,
2. MX-1361 does not contribute to toxicity in the effluent of activated sludge systems and cannot be detected in the effluents of activated sludge systems.

EXPERIMENTAL

Analytical Tests

Chemical analyses were done according to Standard Methods (1) except that color determinations were made according to an NCASI recommended procedure (2).

The settling tests were performed according to standard procedures (3) except that a 6-rph stirrer was placed in the graduated cylinder to assist settling. The SVI test was done according to Standard Methods (1).

Bioassays were conducted using Daphnia magna cultured in the Institute's laboratory for over 100 generations. Procedures were in agreement with guidelines set forth by the U.S. EPA (4). Specific procedural details are presented in Table 4.

Biological Treatment

Biological treatment was performed in 3 liter completely mixed activated sludge reactors for 31 days. Each reactor was baffled and mechanically stirred to ensure complete mixing. Air was metered through a water-filled gas washing bottle to minimize evaporation losses in the reactors. The reactors were fed at a rate of 12 L/day, producing a hydraulic residense time of 6 hours. The MCRT was controlled by daily wasting of sludge directly from the reactor. The nominal MCRT was 8 days.

TABLE 4

Details of Bioassay Tests

Test Chambers:	250-mL beakers, 5 organisms per beaker
Life Stage Tested:	Neonate, less than 24 hours old
Number of Test Organisms:	20 neonates per concentration
Dilution Water Source:	Lake Winnebago (lower Fox River head waters) water filtered through 0.45µm glass fiber filter
Test Duration:	48 hours
Aeration:	None during experiment, dilution water near saturation at outset of experiment
Water Hardness:	167 mg/L as $CaCO_3$
Sample Adjustment for pH:	None; samples used as received
Pretest Storage:	None
Monitored Parameters:	Dissolved oxygen, pH, temperature and % survival of test organisms
Feeding:	Test organisms were not fed during the experiment

A minimum level of dissolved oxygen of 1.0 mg/L was maintained in the reactors, and concentrations of 1.0 mg/L nitrogen and 0.5 mg/L phosphorus were maintained in the effluent to prevent nutrient limitations.

The reactors were operated until a steady-state condition, as judged by stable effluent quality over time, was reached. Samples were then taken for analyses.

Enzyme Preparation

The enzyme preparation is derived from a bacterium. The enzyme is capable of depolymerizing levan, a major component of bacterial slimes. The enzyme preparation cannot reduce cellulose, hemicellulose, starch, or dextrin; it does have a low level of proteolytic activity.

Acknowledgment

We thank Messrs Dennis Van Rooy and James E. Beatty of Appleton Paper's Combined Locks mill for the effluent samples used in this study.

We also thank Mr. Arthur A. Webb and Miss Sally A. Berben of IPC for laboratory assistance.

REFERENCES

1. APHA, AWWA, and WPCF, Standard Methods for the Examination of Water Wastewater, 14th Edition, (1976).

2. "An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color", NCASI Technical Bulletin No. 253 (December, 1971).

3. Vesilind, P., Treatment and Disposal of Wastewater Sludges, Ann Arbor Science, Ann Arbor, Michigan (1974).

4. Peltier, W., "Methods for measuring the acute toxicity of effluents to aquatic organisms", U.S. EPA Report No. EPA 600/4-28-012 (January, 1978).